CO TOLERANCE OF PD RICH PLATINUM PALLADIUM CARBON SUPPORTED ELECTROCATALYSTS FOR PEMFC APPLICATIONS

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Abstract

The potential use of carbon supported PtPd$_y$ ($y=1-6$) electrocatalysts as CO tolerant anodes for proton exchange membrane fuel cell (PEMFC) applications has been investigated in the present study. Cyclic voltammetry experiments at 80 °C, the operating temperature of the PEMFC, reveal that upon CO saturation, a lower fraction of surface sites are poisoned in the case of PtPd$_y$ compared to Pt, resulting in higher amounts of adsorbed hydrogen. Fuel cell tests demonstrated that the need of reasonable hydrogen oxidation currents with and without CO necessitates the presence of Pt in the catalyst. As a CO tolerant PEMFC anode catalyst, PtPd$_y$ attains improved performance compared to both Pt and PtRu.

Keywords

PEMFC; CO; PtPd; Electro catalysts.
1. INTRODUCTION

Further advancement in the technology of PEM fuel cells (PEMFC) is essential for the development of an efficient power source for electric vehicles or residential applications. For many practical reasons, the hydrogen for the fuel cell anode is obtained by processing fossil fuels, such as methane and gasoline. The product gas in these processes contains more or less carbon monoxide, to which the PEMFC is extremely sensitive. This occurs since the most commonly used electrocatalyst, Pt/C, is susceptible to CO poisoning. In order to overcome this problem, the electrocatalysts ability to poison CO adsorption and/or oxidize it at a low overpotential has to be enhanced, while retaining its hydrogen oxidation capability. It is well established that bimetallic systems, with Pt as one of the components, give substantial tolerance compared to Pt alone to the presence of CO in the fuel stream.

Another noble metal of high catalytic activity is Pd, which is used in a number of industrially relevant reactions [1], although not to the same extent as Pt. Palladium is a very good electrocatalyst for organic fuel electro-oxidation [2] and has the remarkable ability to store and release substantial amounts of hydrogen [3]. While voltammetry studies have indicated stronger CO bonding on Pd [4], as predicted [5], a recent study [6] has shown that the release of hydrogen occluded in palladium may provide a viable route of lowering the surface concentration of adsorbed CO.

The PtPd bimetallic system has also been found to exhibit a high resistance against CO poisoning from the oxidation of formic acid [7-9]. Stonehart [10,11] has proposed PtPd alloys, as suitable electrocatalysts for phosphoric acid fuel cells for hydrogen oxidation. According to his study, the alloys were more tolerant than platinum alone, were resistant to ‘sintering’, and in addition, they could be prepared
with a very high surface area. An extensive examination of the PtPd alloy system showed that a minimum in hydrogen polarization, for constant current density, was obtained at the 50-50 a/o levels [11]. PtPd alloys though, have been found to give inferior performance to Pt in the PEMFC [12].

In the present study, the CO tolerance of the PtPd system is examined. Since exploratory experiments conducted in our lab in the past revealed extremely poor performance for PtPd catalysts with up to 50 a% Pd, only Pd rich electrocatalysts, supported on high-surface area carbon, doped with Nafion, have been prepared. CO stripping experiments and direct measurements under operational conditions in a PEMFC were conducted and showed promising results in comparison to platinum and more importantly to PtRu, the current catalyst of choice.

2. EXPERIMENTAL

2.1 Catalyst preparation and characterization

PtPd catalysts, supported on carbon Vulcan XC-72 with a 20 wt% metal loading, were prepared by a process relative to the one claimed by Degussa AG for PtRu [13]. Deposition of the metals from aqueous solution took place by chemical reduction of their corresponding salts, with platinum nitrate (Merck) and palladium chloride (Aldrich) used as precursors and formaldelhyde as the reducing agent. The catalysts were dried at 80 °C. For PtRu, the lack of high temperature annealing, during the preparation, leads to the noble metals being present in highly dispersed form on the support material without being alloyed to each other, as verified by X-ray diffraction analysis (XRD) [13].
The bulk composition of each of the prepared catalysts was evaluated by energy dispersive X-ray (EDX) analysis, with Pd/Pt ratios ranging from 1 to 6. A crystallite size of 1.7 ± 0.3 nm was estimated for one of the catalysts (PtPd) by XRD, but no accurate differentiation could be made between Pd, Pt or a Pt-Pd solid solution due to a large line broadening observed.

For comparison, PtRu (1:1) prepared by the same method with a Ruthenium chloride hydrate precursor, E-TEK Pt and E-TEK PtRu (1:1), all 20 wt% on Vulcan XC-72, were also used. For the cyclic voltammetry and fuel cell test experiments, propanol based catalyst inks were prepared with Nafion (5%, EW 1100).

2.2 Cyclic voltammetry

Cyclic voltammetry experiments were conducted in 1N H₂SO₄ (Merck) prepared with Millipore super Q water. The setup consisted of a standard electrochemical cell, with the usual three electrode arrangement, on a computer controlled Autolab PGSTAT 20 potentiostat / galvanostat (Ecochemie). The working electrode was prepared by the deposition of the catalyst ink under investigation on both sides of a platinum foil (1.5 cm²), followed by drying in ambient conditions. A platinized Pt square foil (1.5 cm²) was used for counter electrode. Hg / Hg₂SO₄ (K₂SO₄ saturated) was used as a reference electrode, which has a potential of E = +0.658 V versus the Reversible Hydrogen Electrode (RHE) and all potentials were referred to the RHE.

The samples were electrochemically cleaned in solution by continuous cycling between 18 and 960 mV (four cycles), followed by a couple of additional scans between 18 and 1260 mV and nitrogen purging, which was found to ensure stability in terms of surface area response to potential cycling. No dissolution effects for Pd were observed after this treatment. 10% CO in Argon gas (Scott Specialty Gases) was
employed. The solution was saturated with the gas, in each case, while the electrode was held at the adsorption potential, which was 18 mV versus RHE. This adsorption potential is representative for the interaction of CO with a hydrogen saturated surface in a PEM fuel cell. Solution saturation occurred after dosing for about 35 minutes. After each dose the solution was cleaned of any contaminants by bubbling nitrogen through it. Stripping voltammograms were collected between 18 mV (starting potential) and 1.26 V with a scan rate of 5 mV / s, for 25 and 80 °C respectively. Complete oxidation was accomplished in a single scan; no oxidation was monitored during the second scan.

2.3 Fuel cell MEA preparation and experiments

In all fuel cell experiments reported in this paper, Nafion 105 was used as a membrane, and prefabricated 0.35 mg Pt / cm² single sided ELAT gas diffusion electrode from E-TEK was used for the cathode. For the anode a catalyst ink was applied on to an E-TEK single sided ELAT gas diffusion backing resulting in an electrode with a low precious metal loading (0.35 mg / cm²). The electrodes that were used were impregnated with a 5% Nafion solution resulting in a Nafion loading of ~1 mg / cm². Membrane Electrode Assemblies (MEAs) were prepared by hot-pressing the Nafion membrane and the two 7 cm² electrodes together at a temperature of 130 °C and a pressure of 40 bar(g) for 1.5 min.

The MEAs were clamped between two serpentine-machined graphite blocks and connected to the test station. At start-up, a constant voltage of 0.5 V was applied for 18 h, using air (cathode) and hydrogen (anode) humidified at cell temperature by membrane humidification and at a pressure of 1.5 bar. The hydrogen and air stoichiometries were set at 1.5 and 2.0 respectively. All experiments were performed at 80 °C. To examine CO tolerance, the fuel cell’s voltage drop over the electronic load
was kept constant at 0.5 V, while the current density was measured for several CO concentrations in pure H₂, with performance data obtained in the steady state.

3. RESULTS AND DISCUSSION

3.1 Cyclic Voltammetry

Cyclic voltammetry is probably the most widely used technique for the electrochemical characterization of catalysts. Figure 1 compares the voltammograms of supported PtPd(1:1) to Pt and Pd in pure 1 N H₂SO₄ at 25 ºC. The Pt catalyst shows the well known hydrogen adsorption / desorption characteristics for carbon supported platinum [14]; three anodic desorption peaks and two cathodic adsorption peaks assigned to weakly and strongly bonded hydrogen adatoms. Perfect reversibility in the hydrogen region is rarely observed in electrodes consisting of highly dispersed platinum particles on high surface area carbon supports. Both the particle size distribution of the Pt particles, the capacitive current of the carbon support and possibly local mass transport phenomena in small pores contribute to the diversion of this reversibility, especially at practical scan rates. For Pd, additional contributions from (bi)sulfate anion adsorption and from hydrogen absorbed into the Pd lattice are anticipated, in this potential region [15]. The latter effect is not that pronounced since the tendency to form this hydride phase decreases with increasing dispersion of Pd in supported catalysts [16]. The hydrogen region resembles that reported elsewhere for Pd / C [4] and for Pd plated on platinum [17]. These peaks are merged into one for PtPd in the anodic scan. This compares favorably to what has been observed for palladized platinum electrodes [9]. Anion adsorption takes place at less positive potentials on Pd than on platinum, as verified by FTIR experiments on Pd-Pt(111) electrodes in sulfuric
acid solutions [18]. The double layer charges are more compressed for the bimetallic system compared to Pt, as seen in Figure 1. Oxide formation occurs at about the same potential, with the oxide layer reduced in a single peak in the cathodic scan. This is evident from the first cycle. The fact that the oxide reduction profile is a composite of both metals, rather than the sum of the individual contributions, is indication for the existence of an alloy phase [19].

![Cyclic voltammetry of carbon supported Pt, Pd and PtPd in 1 N H₂SO₄ at 25 °C. Scanning rate v= 5 mV / sec.](image)

**Figure 1**: Cyclic voltammetry of carbon supported Pt, Pd and PtPd in 1 N H₂SO₄ at 25 °C. Scanning rate v= 5 mV / sec.

Surface area response was relatively stable for the PtPdₓ catalysts with no decrease in surface process charges observed after ten repetitive cycles, at this temperature. The emergence of an extra sharp peak in the hydrogen region with cycling, as seen for electrodeposited nanostructured PtPd films, believed to be a consequence of the dissolution and the replating of the Pd during cycling leading to the
Figure 2: Cyclic voltammetry of carbon supported Pt, PtPd, PtPd$_6$ and Pd, after CO saturation, in 1 N H$_2$SO$_4$ at 25 °C. Scanning rate ν= 5 mV / sec.

formation of islands of Pd [20], was not observed in the present study. While pure Pd/C is less stable, due to dissolution, no decrease was seen for platinum, as expected. It has to be noted that the reduction peak for the E-TEK Pt catalyst is broader than both palladium and the bimetallic system, pointing to a smaller crystallite size distribution for the prepared catalysts compared to platinum.

Anodic stripping voltammetry was utilized for the study of the electrodeoxidation characteristics of adsorbed CO. Figure 2 shows the CO stripping voltammetry on Pt, PtPd, PtPd$_6$ and Pd, following carbon monoxide saturation at 18 mV vs. RHE and subsequent purging of the solution with N$_2$, at 25 °C. At the adsorption potential of 18 mV the coverage of adsorbed hydrogen is unity. Upon CO saturation of the solution, CO displaces almost all of the hydrogen from the surface, as seen by the significant
Figure 3: Cyclic voltammetry of clean at 25 °C and CO saturated carbon supported PtPd4 at 25 and 80 °C, in 1 N H2SO4. Scanning rate v = 5 mV / sec.

suppression of the adsorption – desorption charges. In all cases, apart for the main oxidation peak, there is a minor ‘pre-wave’ peak, at a lower potential, a result of the oxidation of weakly bonded CO. The main peak potential moves to more anodic values as the Pd composition is increased in the catalyst, which is indicative of the stronger CO bonding on Pd. In addition, stronger anion adsorption on Pd could also play a role in diminishing the oxidation reaction rate [18].

For carbon supported Pt, the limited particle size was found to favor the formation of a linearly bonded species, with the CO molecule occupying an atop site [21]. Bridge bonded CO is the predominant species on palladium [22]. While CO from PtPd originates from both Pt and Pd atoms, the oxidation evolves mainly in a single uniform peak. A synergistic effect is thus evident with the peak not being simply an
addition of the fractional contributions of Pt and Pd sites. Electronic modification of the 
CO adsorption characteristics on the two metals, due to bimetallic particle formation, is 
expected. In alloys, the electron affinity of Pt is significantly higher than that of Pd, 
leading to electron density transfer from Pd to Pt [23, 24], which results in a weakening 
and strengthening of the CO bond with Pd and Pt respectively.

The effect of temperature on the stripping characteristics was also examined. 
With increasing temperature the peak shifts negatively as seen in Figure 3 for PtPd₄, in 
agreement with the general trend of the electro-oxidation rate increasing at fixed 
potential with increasing temperature [21]. At 80 °C the CO peak is smaller with the 
oxidation charge decreased. Additionally, the hydrogen region is not totally suppressed,

Figure 4: Cyclic voltammograms for carbon supported PtPd₆ in 1 N H₂SO₄, after CO 
saturation at 18 mV and 308 mV. The clean spectrum is also depicted for comparison. 
Scanning rate v= 5 mV / sec, Temperature T = 80 °C.
which implies that CO does not fully saturate the surface at this temperature. Similar results were observed for all the catalysts tested. A comparison of the voltammograms for PtPd$_6$/C after CO saturation at 18 mV and 308 mV is shown in Figure 4. Purging of the solution with nitrogen at the respective adsorption potential before starting the potential sweep at 18 mV followed CO saturation. The peak in the hydrogen region, seen in the anodic scan, does not disappear upon CO adsorption at 308 mV. It is due to the evolution of hydrogen from vacant surface sites left unpoisoned by pre-adsorbed CO rather than to the oxidation of very weakly bonded CO. CO chemisorption is independent of potential.

A relative ratio of the catalyst sites poisoned by carbon monoxide ($\theta_{CO}$) can be given by ($Q_{Ho} - Q_{Ha} / Q_{Ho}$) where $Q_{Ho}$ and $Q_{Ha}$ are the charges transferred during the anodic scan in the hydrogen region. It should be noted that due to possible contributions from subsurface hydrogen oxidation from palladium, a direct assignment to surface CO coverage based on these values alone would be rather inaccurate. The values, alongside those of the main peak potentials for CO oxidation are listed, for all catalysts tested at 25 and 80 °C.

<table>
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<th>Catalyst</th>
<th>$E_{\text{main peak}}$ (mV)</th>
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<tr>
<td></td>
<td>25°C</td>
<td>80°C</td>
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<tr>
<td>Pt</td>
<td>718</td>
<td>557</td>
</tr>
<tr>
<td>PtPd</td>
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<td>651</td>
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<tr>
<td>Pd</td>
<td>852</td>
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**Table1:** Main peak potentials ($E_{\text{main peak}}$) and relative ratios of catalyst sites poisoned by CO ($Q_{Ho} - Q_{Ha} / Q_{Ho}$), for a series of catalysts tested at 25 and 80 °C.
25 °C and 80 °C, in Table 1. For 25 °C, only a very small portion of PtPd, remains unpoisoned after CO saturation. Alvarez et. al. observed a slight decrease of the CO coverage on palladium-covered Pt(111) electrodes, compared to Pt(111) [18,25], while Lucas et. al. found the coverage to be identical for the same system [26]. At elevated temperature (80 °C) a more pronounced effect is observed. Whereas the surface of the Pt particles for Pt/C remains fully blocked by CO, the CO coverage decreases with increasing Pd content, with CO displacing 73 % of the hydrogen from Pd/C. This corresponds to the observed decrease of CO oxidation charge, both consistent with a reduction of the saturation coverage of carbon monoxide on Pd. A similar temperature effect has been also observed on carbon supported PdAu electrocatalysts [27].

A lower CO steady-state surface coverage leads to a fraction of the surface open to hydrogen adsorption and subsequent oxidation, crucial for maintaining improved tolerance. Since PEM fuel cells work at about 80 °C, it would be interesting to see how our observations correlate with the influence of CO on PtPdx/C anodes directly under PEMFC operating conditions.

3.2 Fuel cell tests

The voltage / current characteristics, with pure hydrogen as the fuel, of the samples prepared are depicted in Figure 5. Similar j / V characteristics to Pt are attained, with small deviations occurring, especially at higher current densities, as the Pd/Pt fraction increases. In contrast, carbon supported Pd performs poorly compared to Pt. Thus even a small amount of Pt in the catalyst is considered necessary, but also enough to enhance a comparable PEMFC performance to that of a platinum anode.
Figure 5: Current density – cell voltage curves of cells operated on pure H\textsubscript{2} with anode catalysts consisting of carbon supported Pt (E-TEK), PtPd, PtPd\textsubscript{2}, PtPd\textsubscript{4}, PtPd\textsubscript{6} and Pd at a pressure of 1.5 bar. T\textsubscript{cell} = T\textsubscript{hum} = 80 °C.

The effect of CO on the cell performance can be seen in Figure 6, where current density is plotted against concentration, with the cell voltage set at 0.5 V at 80 °C. As expected, very low currents are obtained from Pd, which are totally suppressed by the inclusion of even small concentrations of CO and Pt exhibits its established susceptibility to carbon monoxide poisoning. PtPd\textsubscript{y} containing anodes give comparable, albeit slightly lower, hydrogen oxidation current densities, but with a drop in values that is well improved compared to the metals alone. A better measure of the observed tolerance is given by plotting the percentage of current density to CO concentration, as shown in Figure 7. It is obvious that the inclusion of palladium in the anode electocatalyst leads to enhanced tolerance to CO. There seems to be only a minor
dependence on the fraction of Pd in the catalyst, with a deviation of 5% at 100 ppm. The (1:4) fraction exhibits the best performance, especially at higher concentrations.

Figure 6: Current density versus CO concentration for cells operated with anode catalysts consisting of carbon supported Pt (E-TEK), PtPd, PtPd₂, PtPd₄, PtPd₆ and Pd at a pressure of 1.5 bar and a cell voltage of 0.5 V. T_{cell} = T_{hum} = 80 °C.

with a 47% of the original current obtained in pure hydrogen lost due to the inclusion of 240 ppm of CO in the fuel. Duplicate experiments have shown these results to be reproducible.

Based on the results obtained by stripping voltammetry, presented in the previous section, the inhibition of the poisoning effects could be attributed to the inability of carbon monoxide to fully block vacant sites for hydrogen adsorption and eventual oxidation on the bimetallic catalyst. This stems from the lower CO saturation coverage observed. The solitary use of Pd leads to deteriorating activity in pure hydrogen, which is further suppressed in the presence of CO. It is evident from our
Figure 7: Current density ratios \( j / j_0 \), where \( j_0 \) is the current density obtained in pure H\(_2\), versus CO concentration for cells operated with anode catalysts consisting of carbon supported Pt (E-TEK), PtPd, PtPd\(_2\), PtPd\(_4\), and PtPd\(_6\) at a pressure of 1.5 bar and a cell voltage of 0.5 V. \( T_{\text{cell}} = T_{\text{hum}} = 80^\circ\text{C} \).

results that in the case of PtPd\(_y\) both Pt and Pd atoms contribute to the activity. Hydrogen oxidation should more effectively proceed on Pt, so in principle it is the accessibility of free Pt sites that is most important. This seems to be guaranteed by an overall decrease of CO coverage on the catalyst particles, which is induced by electronic effects. Moreover, Pd can also act as a supplier of hydrogen atoms, by providing vacant adjacent sites for hydrogen molecules to dissociate. As for the role of adsorbed hydrogen incorporated into the Pd lattice, at a typical fuel cell anode operating near +50 mV, it is not expected to be of the highest importance, especially when considering the low amount of adsorbed hydrogen in the nanoparticles.
The activity achieved is compared to that attained from a carbon supported PtRu catalyst (E-TEK), for which X-ray diffraction analysis has confirmed the formation of a uniform Pt-Ru alloy phase with an average crystallite particle size of 2 – 4 nm [28]. The current state of the art is based on this system. The comparison is depicted in Figure 8, which includes a PtRu catalyst prepared at ECN constituting of non-alloyed particles with suggested better oxidation properties [13]. The prepared PtRu exhibits slightly higher current densities for CO concentrations up to 100 ppm, compared to the alloyed system. For higher concentrations the poisoning effects are similar. PtPd₄ on the other hand exhibits enhanced tolerance to carbon monoxide.

**Figure 8:** Current density ratios $j / j_o$, where $j_o$ is the current density obtained in pure H₂, versus CO concentration for cells operated with anode catalysts consisting of carbon supported PtRu (E-TEK), PtPd₄, and prepared PtRu at a pressure of 1.5 bar and a cell voltage of 0.5 V. $T_{cell} = T_{hum} = 80 \, ^\circ C$. 

$V_{cell} = 0.5 \, V$
poisoning, which improves with higher amounts of CO in the fuel stream. An improvement in current density close to 15% is seen for concentrations higher than 200 ppm. This comes to show that palladium rich PtPd electrocatalysts are definitely promising candidates in replacing PtRu for PEM fuel cell applications.

Similar conclusions have been drawn for the use of PtPd in phosphoric acid fuel cells [10,11]. Previous reports on the use of PtPd alloys, as reformate tolerant catalysts, in the PEM fuel cell, unfortunately, have not been encouraging [12]. In the current study, excellent particle size distributions are attained but the extent of alloy formation was not determined for the “as prepared” catalysts. Alloy formation, through extensive annealing at high temperature, could have detrimental effects on the tolerance mechanism, through surface segregation or particle growth effects for instance. Further experiments are needed in order to resolve this.
4. CONCLUSIONS

The effects of CO poisoning on carbon supported, palladium rich, PtPd anode electrocatalysts were examined by cyclic voltammetry and fuel cell tests. CO stripping voltammetry reveals that at 80 °C, the operating temperature of the PEM fuel cell, while CO saturation leads to the total displacement of adsorbed hydrogen from Pt, the inclusion of Pd leads to a reduction of the saturation coverage of CO. By increasing the Pd content this effect becomes more pronounced. Fuel cell anodes consisting of PtPdy catalysts exhibit enhanced CO tolerance compared to Pt, under operating conditions, with PtPd4 providing the best results. More importantly, improved performance to PtRu is demonstrated, with 100 ppm or more of CO in the fuel stream.

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6. REFERENCES


